09926620

PCT

…LD INTELLECTUAL PROPERTY ORGANIZATIO…
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : **C01D 1/28, 1/32, B01D 61/02, C07C 227/40, 229/16**

A1

(11) International Publication Number: **WO 95/27681**

(43) International Publication Date: 19 October 1995 (19.10.95)

(21) International Application Number: PCT/EP95/01277

(22) International Filing Date: 7 April 1995 (07.04.95)

(30) Priority Data:
109249 7 April 1994 (07.04.94) IL

(71) Applicant *(for all designated States except US)*: MEMBRANE PRODUCTS KIRYAT WEIZMANN LTD. [IL/IL]; P.O.Box 138, Rehovot 76101 (IL).

(71) Applicant *(for GB only)*: WHALLEY, Kevin [GB/GB]; 57-60 Lincoln's Inn Fields, London WC2A 3LS (GB).

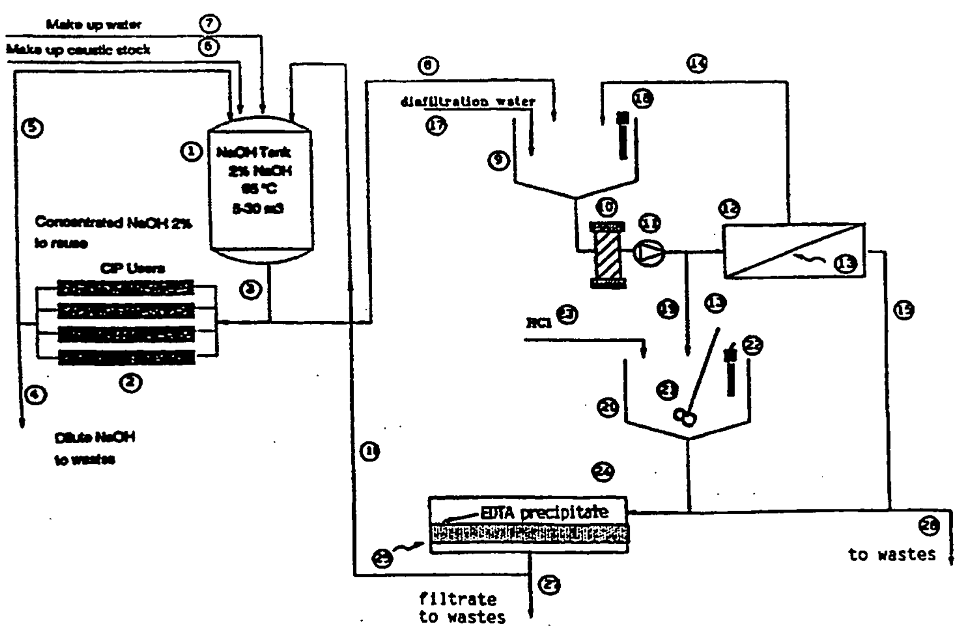
(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: YACUBOWICZ, Henia [IL/IL]; Abarbanel 14, Rishon Lezion (IL). YACUBOWICZ, Jorge [IL/IL]; Abarbanel 14, Rishon Lezion (IL). KATRARO, Reuven [IL/IL]; Prof. Gevaryahu 4, Rishon Lezion (IL). PERRY, Motty [IL/IL]; Kaf-Zayin Benissan 4, Petach-Tikva (IL).

(74) Agent: ABLEWHITE, Alan, James; Marks & Clerk, 57-60 Lincoln's Inn Fields, London WC2A 3LS (GB).

(81) Designated States: BR, CA, JP, MX, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: PROCESS AND SYSTEM FOR PURIFYING A CONTAMINATED CAUSTIC FEED SOLUTION



(57) Abstract

The invention provides a process for purifying a contaminated caustic feed solution (3) to recover spent hydroxide and, optionally, chelating agents, therefrom for reuse, comprising applying the feed solution at a super-atmospheric pressure to the feed side of an alkali-resistant nanofiltration membrane (13), which is permeable to NaOH and KOH while slightly or non-permeable to low molecular weight soluble organic compounds having a molecular weight of at least 150, whereby purified caustic solution (15) is passed across the membrane to the permeate side thereof.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgystan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

PROCESS AND SYSTEM FOR PURIFYING A CONTAMINATED CAUSTIC FEED SOLUTION

The present invention relates to a process and system for purifying a contaminated caustic feed solution to recover spent hydroxide therefrom for reuse.

More specifically, the present invention relates to a process and system that can be used for recovering spent NaOH or KOH and spent chelating agents that are used in cleaning in place (CIP) equipment in the food, biotechnological and pharmaceutical industries.

Cleaning in place of the production equipment in dairies and beverage plants is performed routinely at the end of each production cycle, and serves for maintaining the equipment in high hygienic state. The cleaning of the equipment involves several steps:

i) first rinse with water to remove suspended material;
ii) second rinse with hot water for removing material that is loosely attached to the equipment and piping surfaces;
iii) cleaning with hot alkaline cleaner for removing organic deposits; and
iv) an additional rinse with water.

In some CIP installations, the alkaline step is followed with:

v) water rinse;
vi) acid rinse to dissolve mineral deposits, and finally
vii) water rinse and sanitation.

Many types of caustic cleaners contain chelating agents such as ethylene diamine tetraacetic acid (EDTA) and nitrilotriacetic acid (NTA), which form soluble complexes with Ca^{++} and Mg^{++} ions and prevent a formation of insoluble precipitates. In these cases, the use of the acid and the

subsequent water cleaning step can be omitted, resulting in substantial savings of cleaning time and chemicals [D.A. Timperley and C.N.M. Smeulders, Unilever Research Laboratory, Journal of the Society of Dairy Technology, Vol. 40, No. 1, pp. 4-7 (February 1987); and D. A. Timperley and C.N.M. Smeulders, Unilever Research Laboratory, Journal of the Society of Dairy Technology, Vol. 41, No. 1 (February 1988)].

A typical flow sheet of the CIP process in the dairy or beverage plant is shown in Fig. 1 appended hereto. Typically, but without limitations, the caustic cleaner is stored in a tank 1 having a volume of 2-30 m^3, which is heated to a cleaning temperature of 50-85°C before the cleaning step. The caustic solution is circulated by a circulation pump to the CIP users 2 such as tanks, piping, pasteurizers, evaporators, for a predetermined period of time. After completing the cleaning cycle with caustic cleaner, fresh water is introduced, displacing the caustic solution from the equipment. The first fractions of caustic solution that are characterized with high NaOH concentration are recycled back to the storage tank 1 via a return line 5, while the diluted caustic stream is discharged to wastes through line 4. The caustic concentration in tank 1 is maintained constant by adding make-up water 7 and make-up caustic solution 6 thereto. Most of these tasks are performed automatically by means of control equipment such as level meters, conductivity meters, pH meters and control valves (not shown).

After the cleaning step, the contaminated caustic cleaner still contains a high concentration of active caustic solution, and it can be reused three or four times. After these three or four reuse cycles, the caustic solution

cannot be reused again without further treatment, due to the accumulation of a heavy load of dispersed and soluble organic contaminants. At this point, the contents of the caustic tank are neutralized and discharged to waste. The frequency of discharge varies from once per day to once per week. As a result of the discharge, substantial quantities of valuable caustic and additives are lost, causing a substantial financial loss.

Many types of caustic cleaners contain different types of additives, which are used for improving the efficiency of the cleaning step. Antifoams are added to eliminate foam formation by proteins; surfactants are added for improving permeability of the caustic into a solid cake and improving the effectiveness of cleaning; and chelating agents are added in order to form soluble complexes with Ca^{++} and Mg^{++} ions, thus preventing the formation of insoluble precipitates of $CaCO_3$ and $Mg(OH)_2$.

EDTA and NTA are among the most powerful and therefore widely used chelating agents, though other additives such as gluconates and phosphonates, as well as other chelating and/or complexing agents, are also in common use. Examples of such components other than EDTA and NTA are methylene phosphonic acid, sodium heptogluconate, modified polyethoxylate alcohol, glucosides and organic polyelectrolyte anionic dispersants.

Until recently, it was possible to discharge EDTA and NTA into sewage. In several countries in Europe, the U.S.A., and in the Far East, the discharge of these compounds into sewage is either already prohibited, or is under strict regulations of local authorities. Such environmental legislation created a need for a technology

that will enable the removal of these compounds from the spent caustic stream prior to dischage, or that will enable the recycling of both the additives and the hydroxide from the caustic solution. Furthermore, because of the high price of the chelating agents, there is a substantial drive to recover and reuse them. Therefore, additional objectives of the present invention are methods and systems enabling the recovery and recycling of chelating agents such as EDTA and NTA, and, in general, of components such as organic polyelectrolytes, which are soluble in basic solutions but precipitate in acidic solutions.

With the above objectives and the state of the art in mind, according to the present invention there is now provided a process for purifying a contaminated caustic feed solution to recover spent hydroxide and, optionally, chelating agents, therefrom for reuse, comprising applying said feed solution at a superatmospheric pressure to the feed side of an alkali-resistant nanofiltration membrane, which is permeable to NaOH and KOH, while slightly or non-permeable to low molecular weight soluble organic compounds or organic ions having a molecular weight of at least 150, whereby purified caustic solution is passed across the membrane to the permeate side thereof.

The purified caustic solution is passed across the membrane to the permate side thereof, while all of the dispersed organic and mineral contaminants and most of the soluble organic contaminants, as well as chelating agents, complexing agents, surfactants, antifoams and some divalent ion salts, are retained and concentrated on the feed side of the membrane.

The concentration of the caustic stream in the permeate is nearly identical to the concentration of the caustic in the contaminated feed stream, and its purity is adequate for use in the cleaning process. As a result of using such a membrane device, a substantial reduction of caustic consumption in the factory can be achieved. The caustic savings can reach 90-98% of the regular caustic consumption when such a membrane is not used.

In a preferred embodiment of the present invention, the slightly permeable or non-permeable low molecular weight compounds in the concentrate retained on the feed side of the membrane comprise, at least in part, chelating agents, wherein said chelating agents are soluble in caustic conditions but precipitate under acidic conditions between pH 0 to 4.

The invention also provides a process further comprising adjusting the pH to an acid level by adding a mineral acid, wherein, after the chelating agent is precipitated, it is filtered from the solution, optionally washed, and then reused. Preferably, the mineral acid used is HCL, and the chelating agent may be ethylene diamine tetraacetic acid (EDTA) or nitrilotriacetic acid (NTA), or a polyanionic compound containing carboxylic acid groups.

A further object of the invention is the removal from NaOH of carbonate ions that are formed in the caustic solution as a result of a chemical reaction between the atmospheric CO_2 gas and the caustic cleaner. The alkali-stable nanofiltration membranes used in the present invention preferably remove carbonate ions and pass only the active caustic cleaner. This is an important feature, since in a recycling mode there is an expected accumulation of

carbonate salts as a result of the above-mentioned chemical reaction, further resulting in a decrease of the cleaning potency of the caustic cleaner. When the nanofiltration membrane is used in the caustic recovery process, only the pure caustic, which is nearly free of carbonate salts, is recycled to the cleaning step.

When EDTA is used as a chelating agent, it is retained in the retentate loop, where all the other retained organic and mineral compounds are admixed. Because of its economic value, and also because it is becoming prohibited to discharge this compound into sewage, there are high economic and environmental interests in recovery of EDTA from the concentrate and its recycling as active component back to the holding tank.

The separation of EDTA from various waste streams is well-documented in patent and technical literature.

Japanese Patents 63/190,694; 62/178,553; 63/297,348 and 62/292,748 claim a process for the recovery of EDTA from plating wastes. In their process, the pH of the waste stream is adjusted ≤3 with acid, causing free EDTA to precipitate in crystal form.

German Patent 39 29 137 discloses the recovery of EDTA from electroplating wastes by protonating the spent EDTA by means of a bipolar membrane stack.

Japanese Patent 89/149,756 discloses a method for separating EDTA from the mother liquor in separation of rare earth elements. In this process, the metal EDTA complex is treated with acid, to reduce the pH and precipitate 90% of the EDTA as solid crystals. The supernatant is treated with

an acid form of the cation exchange resin that adsorbs the remaining EDTA.

W. Erlman, et al., Galvanotechnik 1990, Vol. 81, No. 4, pp. 1249-58,, describe several methods for recovering EDTA from electroplating wastes, among them chemical precipitation, ion exchange and catalytic photolysis.

Despite the teachings of the above-mentioned references, the recovery of EDTA from the alkaline concentrate of a nanofiltration process has never been disclosed in the literature.

Furthermore, while the precipitation of EDTA by reducing pH to below 3 has been successfully carried out and is described in the above-mentioned literature, direct neutralization of the alkaline concentrate suffers from the following problems:

a) large quantities of acid are needed to neutralize the ≈0.5 Molar solution of caustic; and
b) the presence of a large NaCl concentration leads to high solubility of the EDTA, as compared to the solubility in the salt-free solution. The results of this surprising observation are given in Table 2 hereinbelow.

Thus, the present invention further provides a process as defined above, and further comprising effecting diafiltration of the concentrated feed solution retained on the feed side of the nanofiltration membrane with aqueous solution to decrease the base and salt concentration thereof, and then adjusting the pH to an acidic level whereby organic acetic acid type chelating agents and other

chelating agents which precipitate under acidic conditions contained therein are precipitated and recovered for reuse.

As will now be realized, the above-mentioned problem has now been solved according to the present invention, by removing base and/or salt from the concentrate with water in the so-called diafiltration mode. After this step, the amounts of acid needed for the neutralization are substantially reduced, and the recovery of EDTA is almost complete.

While the above and following descriptions relate to EDTA as the preferred chelating agent, other chelating agents such as NTA can also be recovered according to the present process.

In preferred embodiments of the present invention, the pH of said concentration feed is adjusted to between 0 and 4, and most preferred is a level of between 1 and 3.

The invention also provides a system for purifying a contaminated caustic feed solution containing organic acetic acid chelating agents and organic and mineral impurities, to recover spent hydroxide therefrom for reuse, comprising an alkali-resistant module equipped with an alkali-resistant nanofiltration membrane which is permeable to NaOH and KOH while non-permeable to low molecular weight soluble compounds having a molecular weight of at least 150; means for circulating said feed solution at superatmospheric pressure to the feed side of said membrane; and means for recycling purified caustic solution from the permate side of said membrane for reuse.

Preferably, said system further comprises means for constantly filtering dispersed compounds from concentrated feed solution, thus leaving said concentrate free from suspended matter; means for controlling the conductivity of said concentrate at a predetermined level; diafiltration means for effecting diafiltration of the concentrated feed solution retained on the feed side of said membrane; means for adjusting the pH of the concentrate to a predetermined level; means for filtering precipitated chelates and separating the same from dissolved organic and mineral contaminants retained in said concentrated feed solution; and means for recycling purified caustic solution from the permeate side of said membrane into a further filtering means together with said filtered precipitated chelates.

The invention will now be described in connection with certain preferred embodiments with reference to the following illustrative figures so that it may be more fully understood.

With specific reference now to the figures in detail, it is stressed that the particulars shown are by way of example and for purposes of illustrative discussion of the preferred embodiments of the present invention only, and are presented in the cause of providing what is believed to be the most useful and readily understood description of the principles and conceptual aspects of the invention. In this regard, no attempt is made to show structural details of the invention in more detail than is necessary for a fundamental understanding of the invention, the description taken with the drawings making apparent to those skilled in the art how the several forms of the invention may be embodied in practice.

In the drawings:

Fig. 1 is a flow sheet of a standard cleaning in place process; and

Fig. 2 is a schematic diagram of a preferred process of the present invention.

All of the above-mentioned features and the main embodiments of the present invention are illustrated in a schematic form in Fig. 2, in accordance with the following explanations.

It is possible to run the process of the present invention in the following operational modes: batch, modified batch, and a continuous process.

Referring now to Fig. 2, in the modified batch process a relatively large, fixed volume of solution or suspension, stored in tank 1, is continuously fed into a smaller tank 9 at such a rate that the level in tank 9 is kept constant until the major part of the volume has been removed from tank 1 (for example, 90%). The concentrate is stored in tank 9. One benefit of this approach is that tank 9 can be relatively small; for example, tank 9 may be one-tenth the size of tank 1.

The stream 8 from NaOH holding tank 1, containing caustic and organic contaminants, is continuously introduced into holding tank 9 of the membrane unit. Stream 8 is first filtered at 10 and pumped by pump 11 into membrane module 12, equipped with an alkali-stable nanofiltration membrane 13. The retentate stream 14 is recycled back to holding tank 9, while the permeate 15, free of contaminants, is returned to main holding tank 1 via a return pipe 16. All the contaminants, constituting suspended material, are

separated in filter 10, while the soluble organic and mineral contaminants which were retained by the nanofiltration membrane, as well as chelates, surfactants and anti-foaming agents, are retained in a highly concentrated form in system tank 9. Through the use of this scheme, most of the caustic solution is recycled in a pure form into holding tank 1, while the retained organic and mineral impurities are first processed to recover the chelating agent, such as EDTA, and then discharged through pipe 27 to the waste.

In the batch mode, the whole volume of the caustic tank 1 will be transferred into a large system tank 9 of the same volume. During this process, the volume in tank 9 will decrease as a result of permeate that is removed in membrane module 12. At the end of the concentration run, the feed volume is decreased to a predetermined level, for example, to one-tenth of the starting volume [(VCF>=10; VCF is a volume concentration factor, i.e., the ratio between the initial feed volume and the final feed volume). The concentration of retained species has increased proportionally. After completion of the concentration run, the contents of tank 9 will be transferred via filter 10 to the precipitation tank 20, from which the EDTA will be recovered.

The disadvantage of the batch process is the relatively large size of tank 9.

In the continuous mode, contaminated caustic soda from tank 1 will be continuously pumped into membrane module 12, thus splitting the feed stream into two: the filtered concentrate stream 14 containing EDTA and dissolved organics, and the pure caustic stream 15, which is recycled

back to tank 1. In this mode, concentrate stream 14 is transferred directly to a precipitation tank 20 for the recovery of EDTA (not shown).

In the continuous mode, the need for tank 9 would be eliminated, thus leading to a cost advantage over the batch mode. Plant design, reproducability and reliability of operation are, however, strongly dependent on the constant composition of feed stream 8. Also, the control equipment needed for a continuous process is expensive and must be taken into consideration when choosing the mode of operation.

The above-described modified batch operation is the preferred mode for caustic recovery in CIP operations, because the membrane feed tank 9 can be one-tenth the volume of main caustic tank 1; compared to the batch and continuous modes, the modified batch mode is highly flexible and can be successfully applied, even when the caustic solution composition varies and membrane fluxes change.

Therefore, a further embodiment of the present invention, aimed at recovery and recycling of EDTA, comprises the following steps:

Diafiltration water 17 is added to the membrane unit tank while removing the permeate through lines 15 and 28 into wastes, until the conductivity within tank 9, measured by meter 18, is as low as is needed for the subsequent precipitation. Clear liquid 19 is then transferred into precipitation tank 20, equipped with a pH measuring electrode 22, means 23 for adding acid, and agitator 21. The pH within tank 20 is adjusted to the required level of a range of between 1-3, and the EDTA is left to precipitate.

The whole stream is then passed into filtration unit 24 which contains a suitable filter 25, which retains the precipitated EDTA and discharges the filtrate 27 with the contaminants. Subsequently, the caustic permeate 15 is directed into filter unit 24, causing the EDTA to dissolve and flow into holding tank 1 via piping 16.

The filtration units and filtration membranes used to filter the precipitated EDTA may be any of those well-known in the art. For example, microfilters from 0.1-20 microns, or filter screens, cloths, or nets may be used, all of which may be made from organic or inorganic materials, ceramics, or metal. The actual filter units may be chosen from filter bags, rotary filters, deadend filters, filter presses, tubular, plate, or frame filters.

While the invention will now be described in connection with certain preferred embodiments in the following examples so that aspects thereof may be more fully understood and appreciated, it is not intended to limit the invention to these particular embodiments. On the contrary, it is intended to cover all alternatives, modifications and equivalents as may be included within the scope of the invention as defined by the appended claims. Thus, the following examples which include preferred embodiments will serve to illustrate the practice of this invention, it being understood that the particulars shown are by way of example and for purposes of illustrative discussion of preferred embodiments of the present invention only and are presented in the cause of providing what is believed to be the most useful and readily understood description of formulation procedures as well as of the principles and conceptual aspects of the invention.

EXAMPLE 1

Stability of Nanofiltration Membranes

Example 1 exemplifies the importance of using only base stable nanofiltration membranes, which will pass the base and retain the contaminants and EDTA.

A series of nanofiltration membranes were exposed to a long-term stability experiment in a 5% solution of NaOH at 50°C. Their performance with two test models was determined before and after an immersion test. The results are given in Table 1 below, and demonstrate that the alkali-stable membranes of the MPT-32 and 34 series are indeed alkali-resistant and suitable for applications in alkali streams. Other nanofiltration membranes are not stable, as shown in this example, and may not be used.

TABLE 1

Alkali Stability of Various Nanofiltration Membranes

exp N°	Membrane typ	Performance at start			Performance after immersion for a period of 500 hours in 5%NaOH at 50°C		
		Flux L/m2hr	Rejection to 0,5% EDTA (%)	Rejection to 4% sucrose (%)	Flux (L/m2hr)	Rejection to 0,5 % EDTA (%)	Rejection to 4% sucrose (%)
1	NF-40 Filmtec	60	99	99	120	72	51
2	Desal 5	130	99	99	350	10	5
3	NTR7450	200	99	98	300	70	50
4	MPT -30	100	97	85	190	65	50
5	MPT -31	100	97	85	250	87	65
6	MPT -32	60	99,9	98	100	99	95
7	MPT -34	50	99,9	99	75	99	99

NF-40-Filmtec Corp.:Desal-5 Desal Corp: NTR 7450 Nitto Corp: MPT-MPW CORP:

EXAMPLE 2

EDTA Precipitation and pH

Solutions of 5 grams of disodium EDTA, purchased from Riedel deHaen, dissolved in 100 g water containing different amounts of NaCl at pH ≈ 10, were adjusted to pH = 2 by addition of a few ml of 32% HCl. The solutions were stirred by a magnetic stirrer and the pH was measured by pH electrode. The solutions were stirred for several hours, then filtered across Whatman filter paper No. 41. The concentration of EDTA is the filtrate was measured by means of Ca solution in the presence of Eriochrom Black T

indicator. The results of these measurements are given below in Table 2.

The results show that, at pH = 2, as the amount of salt (NaCl) increases, the amount of EDTA precipitate decreases. If the pH of these solutions is adjusted to pH = 1, then even in the presence of a high salt concentration, most of the EDTA will precipitate. The pH chosen is a function of the concentration of salt and the choice of using a diafiltration mode to remove excess salt and/or base; this is also related to the economics of the quantity of acid needed to adjust the pH. Without the diafiltration mode, and in the presence of salt, the pH should be optimally adjusted to the more acidic range (for example, pH = 1). With the diafiltration mode, the pH may be adjusted to the less acidic range (for example, pH = 3) to obtain a good precipitation of EDTA.

permeate were collected. The permeate was crystal clear and did not contain any colour or suspended material which was originally present in the feed solution. The accumulated concentration of NaOH in the permeate at the end of the experiment was identical to that at the beginning, i.e., 2%. The concentration of EDTA in the permeate was nearly zero at the end of the experiment, compared to ≈0.5% in the feed solution, indicating a rejection value to EDTA of more than 99%. The concentration of EDTA in the concentrated feed solution was 4.99%.

At this point, the experiment was stopped, the cell was opened, and a volume of 20 ml DI water was added into the pressure cell. The concentration experiment was then continued, collecting 20 ml of permeate. This operation was repeated 5 times, each time recording the fluxes and concentrations of NaOH and organics (COD) in the feed.

The results of these experiments are summarized in Table 3, and indicate that during the diafiltration mode described above, the concentration of NaOH was reduced proportionally to the number of diafiltration steps, from 20 to 0.13 g/l.

After step 5, the concentrate solution was removed from the cell into a beaker equipped with a magnetic stirrer and its pH was adjusted to pH < 3 by adding concentrated HCl. The solution was left at room temperature for about one hour while being stirred, following which the EDTA precipitate was filtered out on a Whatman No. 41 filter. The amount of EDTA on the filter paper was 0.765 g of H_4 EDTA, indicating that more than 97% of the EDTA was precipitated by this method.

TABLE 2

Solubility of EDTA in Pure Aqueous Solutions, as Compared to the Solubility in the Presence of Salt

exp Nº	concentration of NaCl in the solution (grams/kg solution)	concentration of EDTA found in the supernatant after precipitation and crystallization (Grams/liter)
1	0.0	1.4
2	10.0	1.9
3	20.0	6.5
4	50.0	29.8
5	100.0	36.3
6	200.0	42.0

EXAMPLE 3

Concentration and Recovery of EDTA from the CIP Stream of a Milk Factory

About 200 ml of spent caustic solution from CIP of a milk factory, containing 2% NaOH, 0.5% Na_2 EDTA-$2H_2O$ (MW 372), suspended and dissolved organic contaminants, was introduced into a laboratory scale pressure cell, equipped with an alkali stable MPT-34 nanofiltration membrane. The cell was connected to a pressurized nitrogen source of 30 bars and operated at this pressure, while stirring with a magnetic stirrer located above the membrane, until 180 ml of

The collected EDTA was then used to make another solution, and the above experiment was repeated in the same way, giving the same results and showing that the EDTA can be recycled.

TABLE 3

Removal of NaOH by Diafiltration

After DF step#	NaOH Concentration [grams/l]	Flux [L/m2h]
1	7.4	30
2	2.7	30
3	1.0	30
4	0.37	30
5	0.13	30

EXAMPLE 4

Removal of Na_2CO_3 from Spent Caustic Solution

200 ml of an aqueous solution containing 2% NaOH and 0.5% Na_2CO_3 was subjected to a separation experiment in a lab cell equipped with a MPT-34 membrane. After filtering 180 ml into the permeate, the concentration of NaOH and Na_2CO_3 was determined in the feed, concentrate, and permeate. The results are given in Table 4 below.

TABLE 4

Separation of Carbonates from NaOH

	Conc in Feed [%]	Conc in Permeate [%]	Conc. in Concentrate [%]	Spot Rejection [%]	*Mass Balance rejection [%]
CaCO3	0.5	0.1	4.1	91.4	82.0
NaOH	2.0	2.0	2.0	0.0	0.10

*In a process concentrating 10 times (VCF = 10)

EXAMPLE 5

Example 3 was repeated, without the diafiltration and adjusting the EDTA concentrate solution to a pH of 1.0. In this mode, 98% of the EDTA was precipitated and collected on filter paper. The EDTA was reused in similar experiments, giving similar results.

EXAMPLE 6

This example concerns purification of a caustic stream and the recovery and reuse of EDTA from a CIP cleaning solution, using commercial cleaning additive SU-560, manufactured by Lever Industries.

180 ml solution of 2% NaOH and 2% SU-560 was prepared and added to a pressure cell containing membranes MPF-34 (a MPW product), concentrated to 18 ml in the cell (VCF = 10. The EDTA rejection was > 99+% and caustic (NaOH) rejection was 0%. The caustic permeate was clear and could be recycled. The pH of the concentrate was adjusted to 1.0 with concentrated HCl. The precipitating EDTA was filtered and dried. The yield of EDTA was 94%. The recovered EDTA was redissolved in the purified caustic solution to repeat this experiment, which gave similar results.

EXAMPLE 7

Example 6 was repeated with the addition of 0.5% milk to the caustic /SU-560 solution. The results showed a clear permeate solution, with 0% rejection to NaOH and >90% recovery of EDTA.

It will be evident to those skilled in the art that the invention is not limited to the details of the foregoing illustrated embodiments and that the present invention may be embodied in other specific forms without departing from the spirit or essential attributes thereof. The present embodiments are therefore to be considered in all respects as illustrative and not restrictive, the scope of the invention being indicated by the appended claims rather than by the foregoing description, and all changes which come within the meaning and range of equivalency of the claims are therefore intended to be embraced therein.

WHAT IS CLAIMED IS:

1. A process for purifying a contaminated caustic feed solution to recover spent hydroxide and, optionally, chelating agents, therefrom for reuse, comprising:

applying said feed solution at a super- atmospheric pressure to the feed side of an alkali-resistant nanofiltration membrane, which is permeable to NaOH and KOH while slightly or non-permeable to low molecular weight soluble organic compounds having a molecular weight of at leaast 150, whereby purified caustic solution is passed across the membrane to the permeate side thereof.

2. A process according to claim 1, wherein the slightly permeable or non-permeable low molecular weight compounds in the concentrate retained on the feed side of the membrane comprise, at least in part, chelating agents, wherein said chelating agents are soluble in caustic conditions but precipitate under acidic conditions.

3. A process according to claim 2, further comprising adjusting the pH to an acid level by adding a mineral acid, wherein after the chelating agent is precipitated, it is filtered from the solution, optionally washed, and then reused.

4. A process according to claim 3, wherein said acid used to precipitate the chelating agent is HCL.

5. A process according to claim 2, wherein said chelating agent is ethylene diamine tetraacetic acid (EDTA).

6. A process according to claim 2, wherein said chelating agent is nitrilotriacetic acid (NTA).

7. A process according to claim 2, wherein the chelating agent is a polyanionic compound containing carboxylc acid groups.

8. A process according to claim 1, comprising effecting diafiltration of the concentrated feed solution retained on the feed side of said membrane with aqueous solution to decrease the base and salt concentration thereof, and then adjusting the pH to an acidic level, whereby organic chelating agents contained therein are precipitated and recovered for reuse.

9. A process according to claim 8, wherein said organic acetic acid chelating agent is ethylene diamine tetraacetic acid (EDTA).

10. A process according to claim 8, wherein said organic acetic acid chelating agent is nitrilotriacetic acid (NTA).

11. A process according to claim 8, wherein the chelating agent is a polyanionic compound containing carboxylic acid groups.

12. A process according to claim 8, wherein the pH of said concentrated feed solution is adjusted to between 0 and 4.

13. A process according to claim 8, wherein the pH of said concentrated feed solution is adjusted to between 1 and 3.

14. A process according to claim 1, wherein said membrane is permeable to NaOH and non-permeable to organic substances characterized with a molecular weight range of 150 to 1000.

15. A process according to claim 1, wherein said membrane is permeable to NaOH and non-permeable to organic substances characterized with a molecular weight range of 150 to 500.

16. A process according to claim 1, wherein said membrane is permeable to NaOH and non-permeable to organic substances characterized with a molecular weight range of 150 to 250.

17. A process according to claim 1, wherein said nanofiltration membrane is substantially non-permeable to carbonate ions, whereby purified caustic solution substantially free of carbonate salts is passed across the membrane to the permeate side thereof.

18. A system for purifying a contaminated caustic feed solution containing chelating agents and organic and mineral impurities, to recover spent hydroxide and, optionally, chelating agents, therefrom for reuse, comprising:

an alkali-resistant module equipped with an alkali-resistant nanofiltration membrane which is permeable to NaOH and KOH while slightly or non-permeable to low molecular weight soluble organic compounds or organic ions having a molecular weight of at least 150;

means for circulating said feed solution at superatmospheric pressure to the feed side of said membrane; and

means for recycling purified caustic solution from the permate side of said membrane for reuse.

19. A system according to claim 18, further comprising:

means for constantly filtering dispersed compounds from concentrated feed solution, thus leaving said concentrate free from suspended matter;

means for controlling the conductivity of said concentrate at a predetermined level;

diafiltration means for effecting diafiltration of the concentrated feed solution retained on the feed side of said membrane;

means for adjusting the pH of the concentrate to a predetermined level;

means for filtering precipitated chelates and separating the same from dissolved organic and mineral contaminants retained in said concentrated feed solution; and

means for recycling purified caustic solution from the permeate side of said membrane into a further filtering means together with said filtered precipitated chelates.

Fig 1.

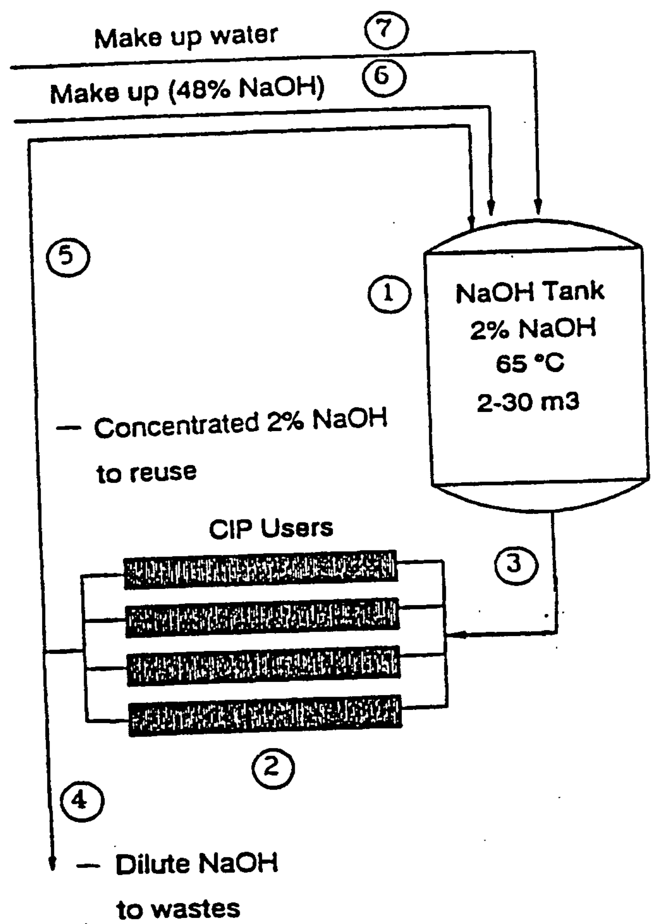
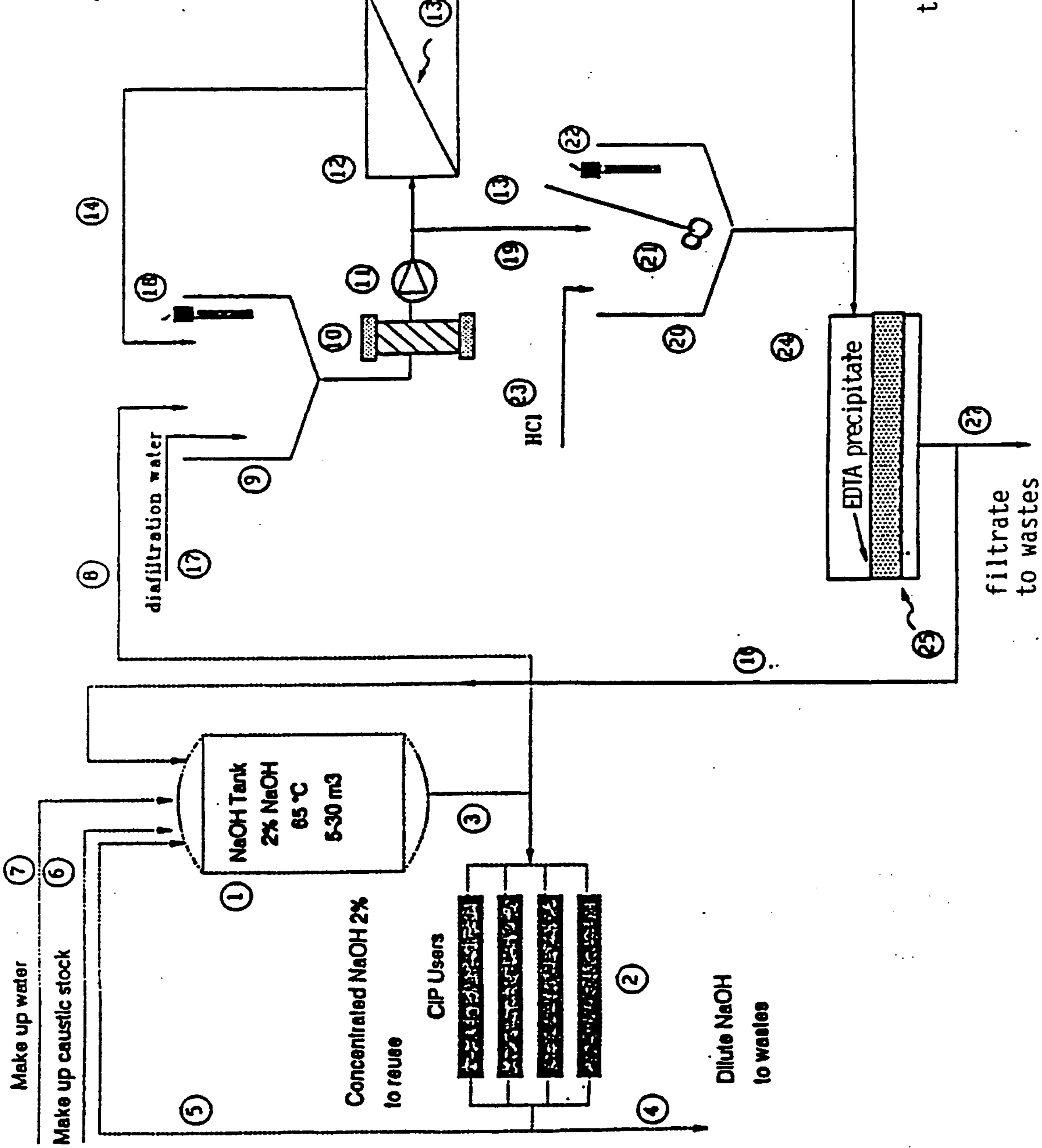

Make up water
7
Make up (48% NaOH)
6
5
1
NaOH Tank
2% NaOH
65 °C
2-30 m3
— Concentrated 2% NaOH
to reuse
CIP Users
3
2
4
— Dilute NaOH
to wastes

Fig 2:


Make up water
Make up caustic stock
NaOH Tank
2% NaOH
65 °C
5-30 m3
Concentrated NaOH 2%
to reuse
CIP Users
Dilute NaOH
to wastes
diafiltration water
HCl
EDTA precipitate
filtrate
to wastes
to wastes

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 95/01277

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C01D1/28 C01D1/32 B01D61/02 C07C227/40 C07C229/16

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C01D B01D C02F C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	FETT WISSENSCHAFT TECHNOLOGIE- FAT SCIENCE TECHNOLOGY, vol. 94, no. 10, 1992 LEINFELDEN ECHTERDINGEN DE, pages 401-403, R. DANZIGER 'Ein Membrantrennverfahren zur NaOH-Rückgewinnung' see the whole document ---	1,18
A	DATABASE WPI Week 8505 Derwent Publications Ltd., London, GB; AN 85-027763 & JP-A-59 222 292 (EBARA INFILCO KK) , 13 December 1984 see abstract ---	1-5,8,9, 12,13

-/--

[X] Further documents are listed in the continuation of box C.

[ ] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

1

Date of the actual completion of the international search	Date of mailing of the international search report
21 August 1995	01.09.95

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3016	Van der Poel, W

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JOURNAL OF THE SOCIETY OF DAIRY TECHNOLOGY, vol. 40, no. 1, February 1987 GB, pages 4-7, D. A. TIMPERLEY, C. N. M. SMEULDERS 'Cleaning of dairy HTST plate heat exchangers: comparison of single- and two-stage procedures' cited in the application see the whole document -----	

1